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16. ABSTRACT
EPA established drinking water regulations for ten inorganic substances and radionuclides that became effective on June 24, 1977. As a result of these new regulations, many communities may be required to construct new treatment facilities or to modify existing ones. This paper on cadmium, lead, and silver is the third of a series that reviews existing treatment technology for meeting the EPA drinking water regulations. The effectiveness of conventional coagulation, lime softening, ion exchange, activated carbon, reverse osmosis, and electrodialysis for the removal of the contaminants are discussed. The information consists of data from a general literature review and EPA's recent work on metals removal by conventional treatment.

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Water Technology

Treatment Technology to Meet the Interim Primary Drinking Water Regulations for Inorganics: Part 3

Thomas J. Sorg, Mihaly Csanady, and Gary S. Logsdon

The third in a series summarizing existing treatment technology to meet the inorganic National Interim Primary Drinking Water Regulations, this report describes current treatment methods for removing cadmium, lead, and silver from drinking water.

Cadmium Removal from Water

Health effects. Cadmium was introduced into the USPHS Drinking Water Standards in 1962[1] because minute amounts of cadmium in the kidneys were suspected of causing adverse renal arterial changes in man. The limit established for rejecting a water supply was 0.01 mg/l; this level was maintained by EPA in the National Interim Primary Drinking Water Regulations (NIPDWR)[2] as the cadmium MCL.

Biologically, cadmium is considered a nonessential, nonbeneficial element of high toxic potential. In addition to its association with cardiovascular disease,[3] particularly hypertension, cadmium poisoning from contaminated food[4] and beverages[5] has been reported. Also, epidemiological studies have linked it with the Itai-itai disease in Japan,[6] a disease characterized by decalcification of bones, proteinuria, glycosuria, increased serum alkaline phosphatase, and other more subjective symptoms.

Chronic oral toxicity studies in rats have shown marked anemia, retarded growth, and, in many instances, death at the 135-mg/l cadmium level of the diet.[7] A maximal "no effect" level was not established, however, because cadmium toxicity was shown to have a dietary relationship. (For example, a low protein diet increased cadmium toxicity.)

A drinking water study also has been done with rats exposed to water containing 0.1 to 1.0 mg/l.[8] No cadmium toxicity effects were noted, but cadmium content in the kidney and liver increased in direct proportion to the dose at all levels.

The exact cadmium exposure level that will cause the earliest signs (proteinuria) of chronic cadmium poisoning is unknown. From animal experiments and human industrial exposure cases, however, a cadmium level of 200 mg/l wet weight in the renal cortex is believed to be associated with proteinuria.[9] To attain this critical level, a daily ingestion of 0.352 mg of cadmium is required for a 50-year period, assuming a 5 per cent gastrointestinal absorption rate. Assuming a diet of 0.075 mg/day, the cadmium MCL for drinking water provides about a fourfold safety factor for a person ingesting 2 litres of water per day, with each litre containing 0.01 mg/l cadmium. This does not consider the contribution from smoking, which can be important.

The National Academy of Science (NAS) reviewed the cadmium health effects data for EPA and also concluded that insufficient data are available for establishing a maximum value for no-observed-adverse-health-effect.[10] NAS pointed out that the USSR and WHO have the same maximum limit, and that at the MCL level drinking water contributes only about 20 per cent of the normal daily adult intake. The NAS did not suggest any change in the present limit.

Cadmium is not expected to pose a serious problem for the water utility industry. Only minute traces have been found in natural waters, generally in areas where lead, copper, and zinc are mined and processed.

Because about one half of all the cadmium metal refined is used in industrial plating operations, more serious potential cadmium problems exist in surface waters receiving wastewater from this industry. Surface water problems should be minimal, however, because cadmium carbonate and hydroxide complexes are very insoluble in water of high pH.

Kropp and Kroner[11] reported that only 40 (2.5 per cent) of 1577 water samples from rivers and lakes in the US collected from 1962 to 1967 contained cadmium. The maximum value was 0.12 mg/l, and the mean was slightly below 0.01 mg/l. In 1970 Durum et al[12] reported that 42 per cent of 720 samples from rivers and lakes in the US had cadmium concentrations of 0.001 to 0.01 mg/l. The data also indicated that the higher cadmium levels generally occurred in areas of high population density.

The 1969 Community Water Supply study[13] showed that only fourteen finished water samples from 967 water supplies had cadmium concentrations at or above 0.01 mg/l. The source of cadmium was probably the distribution system rather than the raw water source, because cadmium is commonly found in combination with lead and zinc. Cadmium is a contaminant of zinc-galvanized iron and any corrosive water provides the potential to dissolve cadmium from distribution pipes into the distribution system.

Cadmium chemistry overview. In the pH range from 4 to 13, cadmium has three major species in natural waters—Cd^{+2}, $CdCO_3$, and $Cd(OH)_2$. In the low pH range the predominant species is the free Cd^{+2} ion. At and below pH 7.0 the solubilities of cadmium carbonate and cadmium hydroxide are very low, but above this pH their solubilities decrease with increasing pH. The solubilities of the two forms of cadmium are dependent on the pH and the carbonate content of the water. Hem[14] indicates that the carbonate form is the less soluble of the two, and a pH adjustment of water having a substantial bicarbonate content would probably lower the cadmium concentration. The precipitation of the carbonate form, however, may be slow in dilute solutions, so that achieving the drinking water MCL concentration could be difficult.

Hem[14] also states that cadmium solubility in a system of $Cd + S + CO_2$

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the radium MCL of 5 pCi/l, which was based in part on a radium concentration-mortality relationship. To maintain a 5-pCi/l MCL will cost an estimated $8.8 million and avert 3.7 fatalities annually, at a cost of $2.4 million per fatality. Larsen calculated that at this rate it would cost $790 billion annually to prevent all fatalities due to malignancies in the US. This is about two thirds of the gross national product. Without any knowledge of cost-effectiveness, it is apparent that the US would find it difficult to afford malignancy mortality reduction costs of this magnitude. Had this MCL been examined from a model approach, the inputs and outputs would have been considered in terms of treatment costs to maintain the MCL as well as costs recovered from the reduced mortality rate.

An appendix to the model study by Singley et al[5] is a report on the "Benefit-Cost Analysis of Cardiovascular Disease and Hardness." It concludes that the role of total dissolved solids in cardiovascular mortality is difficult to assess because there is also significant correlation with other water constituents such as potassium, calcium, magnesium, and hardness, each of which obscures the etiological relation of the other with cardiovascular disease. It also contains a statement closely related to Larsen's findings:

> Although it sometimes appears as though no expenditure is too great in protecting human health and life (consider the cost of maintaining persons on kidney dialysis equipment), most public health programs, due to the limited nature of public funds, must be examined within the benefit-cost framework. Ideally, the benefit-cost analysis should also consider alternative uses of public funds to ensure that they are invested in a manner such that the overall benefits are maximized.

A model approach requires the consideration of all inputs and outputs. Although all of the input values are estimates having varying degrees of confidence, it should not be concluded that the model results would not be significant and therefore the model approach should not be used. Quite the opposite: this is an argument for using the model approach, since it is designed to accommodate changes in input estimates. And as the input data are improved, the model results improve.

Particularly difficult problems arise in estimating health risks and construction costs.

Health effects—past and present. In the past, limits for many of the contaminants listed in the standards were established on the basis of threshold levels; that is, they were established at or below a concentration at which there were no adverse health effects.

Current studies have indicated the presence of potential carcinogens in water. For contaminants that are considered carcinogens, one school of thought contends that there is no safe level: although risk becomes smaller at lower concentrations, some adverse effect is inescapable except by total removal of the contaminants, which is usually impossible. Thus the terms "maximum contaminant level" or "maximum acceptable level" become euphemisms for "acceptable mortality rate." Some may consider this a morbid approach, but it describes the problem.

Human health effects are difficult to determine for contaminants that do have threshold levels; they are even more difficult to determine for contaminants that have no threshold. The most valid data are usually associated with animal experiments, and there is no unanimity of opinion as to how or whether these data can be translated to human health risks, which become the model input for health effects.

In the past, estimates were made of the thresholds of contaminants despite the difficulty in doing so, and estimates of the health risks of carcinogens undoubtedly will also be made despite the difficulty and doubts as to their accuracy.

Water quality improvement cost estimates. In the study described here the problem of developing accurate treatment costs was probably as difficult as that of developing accurate health risks and health costs. Therefore, the problem of estimating a benefit-cost ratio is not solely one of estimating health and health risks. The cost of developing treatment processes, particularly where energy requirements are involved, is also uncertain and difficult to estimate.

Summary

The model approach for estimating benefits derived from water quality improvement programs has been reviewed. A model has been developed for three waterborne diseases to demonstrate the feasibility of such an approach. It is emphasized that the model approach can be used for contaminants other than biological factors. The consideration of health benefits (i.e., reduction in disease costs) during the development of drinking water regulations is important in the decision-making process, even though estimates of risk for a given contaminant may vary considerably. The model approach is particularly useful in this consideration because it can accommodate a variety of input values.

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An annual conference paper selected by the JOURNAL, authored by Edgar A. Jeffrey (Active Member, AWWA), state prog. mgr., wtr. sply. br., USEPA, Dallas, Tex., and J. Edward Singley (Active Member, AWWA), prof., envir. engrg., Univ. of Florida, Gainesville, Fla.

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+ H_2O is below the 0.01-mg/l MCL concentration in the pH range 8.9 to 10.7. At higher pH levels with low carbonate water the predominant cadmium species is $Cd(OH)_2$, the solubility of which is not much below 1 mg/l at pH 10 and is close to 0.4 mg/l at pH 11. These data indicate, therefore, that the controlling cadmium complex is the carbonate form, and that the greatest cadmium removals from water should be achieved in the 9 to 10 pH range by conventional coagulation treatment.

Patterson et al[15] conducted studies on the solubilities of the carbonate and hydroxide forms of cadmium and compared the results to theoretical solubility curves. Although hydroxide test results were in excellent agreement with the predicted solubilities, the results of two carbonate tests were not. The optimum pH for cadmium hydroxide precipitation was 10.4 with the solubility at 0.2 mg/l. The carbonate solubilities for both tests at pH 10 and above were almost identical to those of the hydroxide system. Only below pH 10 was the carbonate effect evident. The authors suggested, therefore, that the phase change occurs at pH 10 rather than at the predicted pH of 12.1. The data showed that above pH 10 the hydroxide complex controls and below pH 10 the carbonate data fall somewhat below the hydroxide solubility curve. The advantage in precipitating cadmium with carbonate rather than hydroxide, as stated by Patterson et al,[15] is that treatment can occur at lower pH without sacrificing effluent quality. The optimum pH for cadmium precipitation was 10.5 for hydroxide (0.60 mg/l cadmium solubility); 10.1 for low carbonate system (0.60 mg/l cadmium solubility); and 7.5 for high carbonate system (1.0 mg/l cadmium solubility). The only problem with carbonate precipitation is that process reaction time is slow, often requiring more than 4 hr.

Gardiner[16,17] studied the chemistry of cadmium in natural waters, specifically the adsorption of cadmium on river mud and naturally occurring solids. Laboratory experiments were run with several river muds composed mainly of clay, silica, and humic material. When small amounts of cadmium (0.002–0.177 mg/l) were added to various river mud solutions and the adsorption of cadmium measured, the proportion of cadmium adsorbed decreased from 46 to 4 per cent with increasing cadmium concentrations. When the cadmium concentration was fixed and the solids content varied, the amount of cadmium adsorbed increased with the amount of solids in solution. Significantly, the rate of adsorption was generally very rapid, with equilibrium frequently reached within the first 2 min.

Gardiner[16] also studied cadmium adsorption by specific materials expected to be present in rivers, such as silica, kaolin, humic acid, fish fecal matter, and plant material. Of these materials, humic acid achieved the best adsorption, leading to the conclusion that humic material is the component of river mud responsible for most adsorption of cadmium in natural waters.

Gardiner[17] calculated the proportion of cadmium present in complex forms (hydroxide, carbonate, chloride, sulfate, humic) and as the free ion, Cd^{+2}, using measured stability constants and composition data of eleven samples of river water and sewage. A known amount of cadmium was added to each sample and the proportion of free ion was measured for comparison to calculated values. For most of the samples there was good agreement between the calculated and measured values, indicating no appreciable formation of complexes other than those mentioned above. The calculated results showed that the highest proportion of dissolved cadmium was the free Cd^{+2} ion (35–92 per cent) and the extent of complexation increased with pH and the amount of sewage effluent in the water. Most of the complexation in sewage and sewage effluent resulted from the humic material (0–39 per cent), with the carbonate complex (4–21 per cent) as the next most prevalent complex. In one unpolluted groundwater sample 92 per cent of the cadmium was present as the free ion Cd^{+2}.

The significance of Gardiner's work to water supply treatment is

1. Cadmium probably will not be found in high concentration in turbid surface waters except when the water is low in pH. Because cadmium will complex with most matter found in river waters, only low cadmium concentrations of the free ion should be found in an undissolved form.

2. All adsorbed cadmium should be removed easily by conventional coagulation treatment if the pH of the water is not depressed below pH 7.0.

3. If dissolved organic complexes are formed in low concentrations, granular activated carbon should achieve higher removals than the conventional coal and sand filter.

4. Cadmium should be more difficult to remove from low-turbidity groundwater than from high-turbidity surface waters.

Treatment methods. Because cadmium is not a frequent problem in drinking water, very few studies have been conducted on its removal. The principal source of information on conventional coagulation and lime softening treatment is laboratory and pilot-plant studies conducted by the Drinking Water Research Div. (DWRD)—formally the Water Supply Research Div.—of the USEPA at the Environmental Research Center in Cincinnati, Ohio. Very limited data exist on the removal of cadmium by other treatment methods, such as ion exchange and reverse osmosis.

Conventional coagulation. DWRD ran laboratory jar tests and pilot-plant studies to determine the effect of various operating parameters on the removal of cadmium from well and river water by alum and ferric sulfate coagulation treatment. Laboratory jar-test studies showed that pH was the most significant variable in removal of cadmium regardless of coagulant. This result was expected, because the previously mentioned chemistry studies had indicated that cadmium solubility decreases with increasing pH from 7 to 9–10.

Coagulation jar-test studies using spiked Ohio River water and Glendale, Ohio, well water were run periodically from July 1974 to November 1976. The results of the studies on the effect of pH are shown in Fig. 1 and 2. Alum and ferric sulfate removals with high alkalinity well water containing 0.03 mg/l of Cd increased from about 10 per cent removal at pH 7 to about 100 per cent at pH 9 (Fig. 1). Although both coagulants exhibited a similar removal trend, ferric sulfate always produced higher removals than alum at the same pH.

When the jar-test studies were repeated on spiked Ohio River water, cadmium removals with ferric sulfate were about the same as for well water. At pH 7 cadmium removal was 20–30 per cent and increased to nearly 100 per cent at pH 8.5–9.0. To about pH 8.0, alum coagulation removals were similar to the well water results, but above this point removals were not reproducible, varying from 20 to 90 per cent (Fig. 2). The nonreproducibility of results can probably be explained by the varying quality of the river water and poor quality of alum floc above pH 8. Analysis of the jar-test results indicated that above pH 8 cadmium removals were dependent on the turbidity of the river water. When the turbidity was low (1–20 tu), cadmium removals reached a maximum of 40–60 per cent around pH 8–8.5 and then decreased with increasing pH. With higher turbidity water (above 20 tu) the removals increased with increasing pH. In no case, however, did alum coagulation achieve more than about 80 per cent removal of cadmium. The reason suggested for the high cadmium removal results with alum coagulation on low-turbidity well water is the higher alkalinity of that water. The alkalinity of the river water was around 50–60 mg/l (as $CaCO_3$) for all jar tests as compared to 200 mg/l (as $CaCO_3$) or higher for the well water.

Pilot-plant tests on removing cadmium by conventional coagulation treatment were conducted with the pilot-plant system and procedures described in Part 2 (JOURNAL AWWA, 70:7:379). The test

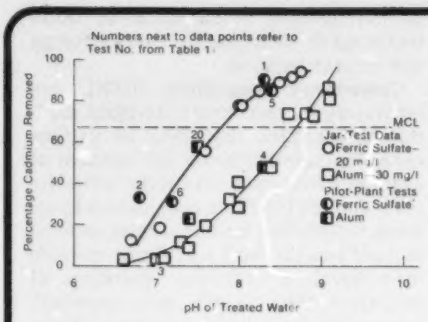

Fig. 1. Effect of pH on Cadmium Removal From Well Water by Coagulation Treatment

Cadmium Concentration—0.03 mg/l

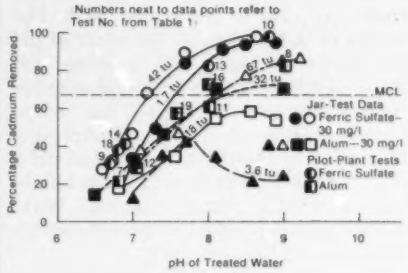

Fig. 2. Effect of pH on Cadmium Removal From River Water by Coagulation Treatment

Cadmium Concentration—0.03 mg/l

TABLE 1

Results of Conventional Coagulation Pilot-Plant Tests for Cadmium Removal

Test No.	Date Started	Length of Test hr	Test Water*	Coagulant Type	Coagulant Dose mg/l	pH of Treated Water	Average Raw Water Concentration mg/l	Percentage Cadmium Removed: Settled Water	Filtered Water: Dual-Media Filter	Filtered Water: Granular Activated Carbon Filters: Virgin GAC†	Exhausted GAC†	Virgin GAC‡
1	10/7/74	104	Cincinnati tap	ferric sulfate	25	8.3	0.029	80	90	–	–	–
2	10/15/74	81	Cincinnati tap	ferric sulfate	25	6.8	0.031	26	33	–	–	–
3	11/11/74	101	Cincinnati tap	alum	26	7.4	0.035	17	23	–	–	–
4	11/18/74	102	Cincinnati tap	alum	26	8.3	0.028	34	48	–	–	–
5	12/9/74	102	Cincinnati tap	ferric sulfate	19	8.4	0.029	67	85	–	–	–
6	12/16/74	101	Cincinnati tap	ferric sulfate	15	7.2	0.032	19	31	–	–	–
7	11/3/75	97	Ohio River	alum	20	6.8	0.027	11	22	41	–	–
8	11/10/75	95	Ohio River	alum	24	9.0	0.036	53	83	92	–	–
9	11/17/75	100	Ohio River	ferric sulfate	25	6.7	0.030	25	31	32	–	–
10	12/1/75	98	Ohio River	ferric sulfate	26	8.8	0.028	76	99	92	–	–
11	12/6/76	102	Ohio River	alum	30	8.0	0.026	46	61	88	88	–
12	12/13/76	100	Ohio River	alum	30	7.0	0.027	7	30	54	69	–
13	2/7/77	93	Ohio River	ferric sulfate	28	8.0	0.032	67	83	94	94	–
14	2/14/77	99	Ohio River	ferric sulfate	31	6.9	0.046	37	41	52	65	–
15	3/14/77	50	Ohio River	ferric sulfate	30	8.7	0.048	94	> 96	> 96	> 96	–
	continuous	50				6.4	0.046	25	25	67	70	–
16	5/9/77	99	Ohio River	alum	30	8.0	0.032	62	73	> 93	> 93	–
17	6/27/77	50	Ohio River	alum	28	7.9	0.040	45	65	–	> 96	> 95
	continuous	45				6.9	0.039	42	36	–	72	64
18	8/1/77	94	Ohio River	ferric sulfate	27	6.8	0.029	31	38	–	76	76
19	11/7/77	91	Ohio River	alum	27	7.7	0.033	46	58	–	> 94	> 94
20	4/3/77	90	well water	alum	33	7.5	0.031	52	58	–	89	81

*Water spiked with $CdCl_2$.
†Filtrasorb 200, Calgon Corp., Pittsburgh, Pa.
‡Hydrodarco 1030, ICI United States, Inc., Wilmington, Del.

waters were Cincinnati tap water; Ohio river water; and Glendale, Ohio, well water. Because none contained naturally occurring cadmium, the waters were spiked with cadmium chloride.

A summary of results of twenty pilot-plant test runs is given in Table 1. The dual-media filter results are also plotted in Fig. 1 and 2 for comparison with jar-test results. Although the test conditions were not always identical, pilot-plant removal results generally agreed with jar-test results. The pilot-plant studies confirmed that cadmium removal is pH dependent and that removals increase with increasing pH from about pH 7 to 9. Furthermore, the data show that ferric sulfate is more effective than alum at the same pH.

Eighteen of the twenty pilot-plant tests were conducted under the same operating conditions from start to finish. To demonstrate more clearly the pH effect on cadmium removal, the pH of the treated water was changed at the midpoint of two test runs, No. 15 and 17. The results of these two test runs, plotted in Fig. 3 and 4, definitely show the effect of changing the pH of the treated water. During the initial 50 hr of each test, when the water was adjusted with soda ash to approximately pH 8.7 (No. 15) and 7.9 (No. 17), cadmium removals by the dual-media filter averaged more than 95 per cent (below the detectable limit of 0.002 mg/l) and 65 per cent, respectively. When pH adjustment was curtailed and the pH dropped below 7, removals also began to decrease very sharply to about 25 per cent for the ferric sulfate test (Fig. 3) and about 36 per cent for the alum test (Fig. 4). The figures also show that alum coagulation did not achieve the MCL at any time and iron coagulation only when the pH was approximately 8.7. If the initial pH of the alum test had been higher, the 0.01-mg/l MCL probably could have been met.

Jar-test studies on the effect of coagulant dose showed that increasing the quantity of alum significantly increased removals, but increasing the ferric sulfate produced only a slight removal increase (Fig. 5). Thus if only a slight increase in cadmium removal is required, it can be achieved by increasing the coagulant dose. This treatment modification is easier and cheaper than adjusting the pH of the raw water.

The studies on the effect of pH and coagulant dose were run with cadmium concentrations of 0.03 mg/l, three times the MCL. To evaluate the effect of higher cadmium concentrations, several jar tests were conducted with cadmium concentrations to 5.0 mg/l. As expected, the higher the cadmium concentration, the lower the percentage of removal even at optimum pH. When the data are plotted to show the amount of cadmium remaining in solution (Fig. 6), the curves indicate that the MCL can be achieved with 30 mg/l of alum if the initial cadmium concentration is about 0.02 mg/l or lower. Because ferric sulfate is more effective than alum, 20 mg/l of this coagulant at optimum pH is capable of achieving the MCL when the initial cadmium concentration is about 0.07 mg/l with well water at pH 8.3–8.7 or about 0.10 mg/l with river water at pH 8.7–8.8.

Lime softening. Cadmium can be removed very effectively from hard water by lime and excess lime softening. Jar-test studies with spiked Glendale, Ohio, well water showed that 0.03 mg/l of

cadmium could be almost entirely removed through the pH range of 8.5 to 11.3 (Fig. 7). Subsequent pilot-plant tests conducted with the same water at pH 9.5 and 11.3 confirmed the excellent removals shown in jar testing. The pilot-plant tests were conducted in the same manner as those described in Part 2 except for test No. 5, in which the pH 11.3 settled water was not recarbonated or settled a second time. The results of the pilot-plant tests are reported in Table 2 and the dual-media filter removals are plotted in Fig. 7 for comparison with the jar-test results.

Because of the excellent removals of 0.03 mg/l of cadmium by lime softening, a jar test was run at pH 11.3 with cadmium concentrations ranging from 0.03 to 10 mg/l. Surprisingly, removals were identical to the initial results: removals near 100 per cent were achieved with all cadmium concentrations, including 10 mg/l. Because the solubility of cadmium hydroxide decreases as the pH increases above 10, high removals were not expected at high cadmium levels. Adsorption onto the calcium carbonate and magnesium hydroxide floc is suggested as the reason for the high removals. Because the test water contained a high concentration of magnesium (21 mg/l), excess lime softening at pH 11.3 produced a voluminous floc that provided an ideal medium for adsorption.

Ion exchange. Standard cation exchange resins are used in the plating industry for removing cadmium from rinse water. Ion exchange, therefore, should be able to remove cadmium from drinking water unless competing cations are much more selective than cadmium. Calmon[18] reported the selectivity of cadmium for a strong-acid cation exchanger (hydrogen form) to be slightly above copper, zinc, and magnesium but below calcium, silver, lead, and barium. One manufacturer of a strong-acid cation exchanger* also indicates that the cadmium selectivity for the exchanger is higher than copper, zinc, magnesium, ferrous ion, and manganese but below calcium, mercury, lead, and barium.[19] The same company also states that in neutral or alkaline solutions cations that form insoluble or slightly insoluble carbonate salts, such as cadmium, are strongly attracted to weak-acid carboxylic resins. Few selectivity data are available, however, for weak-acid cation exchanges. Calmon[18] and Patterson[20] state that claims have been made for the existence of resins specific for cadmium removal.

A general review of the literature showed no studies on the use of ion exchange resins for removing cadmium from drinking water. For wastewater, however, Linstedt et al[21] evaluated the removal of very low concentrations of cadmium from secondary sewage effluent by cation and anion exchange resins in series. The cation column removed 99 per cent of 0.016 mg/l of cadmium in the sewage effluent, suggesting that cadmium could be removed by an ion exchange treatment facility or by a home-size ion exchange unit to control distribution line problems.

Activated carbon. Both powdered activated carbon (PAC) and granular activated carbon (GAC) have some ability to remove cadmium from water. Thiem and O'Connor[21] studied various types of PAC for removing cadmium from a synthetic drinking water. The best removals were 29 and 26 per cent with 100 mg/l of PAC 1* and PAC 2†, respectively, with a solution containing 0.05 mg/l of cadmium at pH 7. Removals increased with increasing pH. At pH 9 and the same carbon dose, cadmium removal with PAC 2 doubled, from 26 to 53 per cent, and removal by PAC 1 rose to 43 per cent. A third PAC material‡ was the least effective of the three. At pH 7 and 9, removals were 7 per cent and 27 per cent, respectively, with a 100-mg/l dose.

The DWRD also ran several experiments for removing cadmium from natural well water and Ohio River water with varying doses of PAC 3. The results were similar to those of Thiem and O'Connor. Very large doses of PAC (200 mg/l) were required for 20–30 per cent removal of 0.02 mg/l or 0.10 mg/l of cadmium from well water at pH 8.1–8.3. Slightly higher removals, 40–50 per cent, were obtained with 0.03 mg/l of cadmium in Ohio River water at pH 7.6–8.4. When the jar tests were repeated with PAC followed by 30 mg/l of alum, only small increases in removal were produced above those accomplished by alum coagulation alone. Because large amounts of PAC removed only small additional amounts of cadmium, the use of PAC is neither practical nor economical for cadmium removal.

DWRD pilot-plant tests used virgin and exhausted GAC filter media in parallel with conventional dual-media filter. The data presented in Tables 1 and 2 suggest that GAC can adsorb cadmium. Except for high pH runs, when high cadmium removals were also achieved with the dual-media filter, cadmium removals for virgin and exhausted GAC filters were always significantly higher than those of the dual-media filter. Cadmium removal by the exhausted GAC filters was equal to or greater than that achieved by the virgin GAC filters.

In addition to the conventional pilot-plant test of GAC filtration, an eight-week series of GAC adsorption experiments was run with GAC 1* and exhausted GAC 2.* Spiked tap water was filtered through each filter column for about 100 hr each week. No coagulant or other chemical was added to the water and the filters were not backwashed between runs. Approximately 48 hr elapsed between tests when the system was shut down for weekends.

Eight or nine water samples were collected during each test run; the average removal value for each test is shown in Table 3. Cadmium reduction ranged from 30 to 7 per cent for GAC 1 and 54 to 17 per cent for exhausted GAC 2. The higher cadmium removals by the exhausted carbon media were consistent with the results achieved in coagulation studies (Table 1). With few exceptions, weekly removal averages showed a decreasing trend for both filters. In contrast, the daily removal results for each test run showed a slightly increasing pattern from Monday to Friday.

Reverse osmosis and electrodialysis. Mixon[23] reported very high cadmium removal from tap water by three laboratory-scale cellulose acetate membranes. Removals higher than 90 and 98 per cent were achieved with water spiked with cadmium concentrations of 0.10 and 0.98 mg/l, respectively. When the tests were repeated with tap water spiked with cadmium in combination with five other metals (Ba, Cr, Cu, Pb, and Zn), no differences in rejection of cadmium were found.

Hindin et al[24] also ran laboratory tests using a very small [7.00 cm (2.75 in.)] diameter reverse osmosis cellulose acetate cell on aqueous solutions spiked with cadmium. Removal results were significantly lower than those reported by Mixon,[23] with only 70 per cent removal achieved with cadmium concentrations of 0.097, 0.950, and 9.250 mg/l. If only 70 per cent removal is achievable by reverse osmosis, this technique would be useful only for cadmium levels about 0.03 mg/l or lower.

Houle[25] reported a full-scale reverse osmosis system for recycle of wastewaters from an electronics manufacturing plant. During an eight-week period, when the influent cadmium concentration varied from 0.024 to 0.059 mg/l, cadmium rejection ranged from 43 to 83 per cent. The average percentage removal was 66 per cent, which is comparable with the laboratory results of Hindin.[24] Houle suggested, however, that the low rejection of cadmium might have resulted from the resolution of the analytical technique used. Because data from these studies indicate cadmium removal of only about 70 per cent, reverse osmo-

*Duolite C-20, Diamond Shamrock Chemical Co., Cleveland, Ohio

*Amoco PX-21, Amoco Research Corp., Chicago, Ill.
†Darco HDP, ICI United States, Inc., Wilmington, Del.
‡Nuchar Aqua, Westvaco Corp., Covington, Va.

*Filtersorb 100 and Filtrasorb 200, respectively, manufactured by Calgon Corp., Pittsburgh, Pa.

TABLE 2

Results of Lime Softening Pilot-Plant Test With Well Water

Test No.	Date Started	Length of Test hr	pH of Treated Water	Raw Water Contaminant*		Percentage Contaminant Removed					
						Settled Water		Filtered Water			
								Dual-Media Filter	Granular Activated Carbon Filters		
				Contaminant	Concentration mg/l	First	Second		Virgin GAC†	Exhausted GAC‡	Virgin GAC§
1	1/20/75	97	11.3	cadmium	0.031	> 95	> 95	> 95	> 95	–	–
2	3/3/75	59	9.5	cadmium	0.030	92	–	> 93	> 93	–	–
3	3/24/75	99	11.3	cadmium	0.028	> 96	> 96	> 96	> 96	–	–
4	11/28/77	91	9.6	cadmium	0.027	> 93	–	> 93	> 93	> 93	> 93
5	12/12/77	87	11.3	cadmium	0.038	> 95	–	> 95	> 95	> 95	> 95
6	12/19/77	105	9.5	lead	0.41	82	–	99	–	99	99
7	3/6/78	94	9.4	silver	0.12	32	–	> 74	–	> 74	> 74
8	3/13/78	96	11.1	silver	0.12	59	–	> 74	–	> 74	> 74

*Water spiked with $CdCl_2$, $PbNO_3$, $AgNO_3$.
†Filtrasorb 100, Calgon Corp., Pittsburgh, Pa.
‡Filtrasorb 200, Calgon Corp., Pittsburgh, Pa.
§Hydrodarco 1030, ICI United States Inc., Wilmington, Del.

TABLE 3

Results of Pilot Tests on Removal of Cadmium by Granular Activated Carbon

Test No.	Length of Test Run hr	Average Raw Water Concentration* mg/l	Average Percentage Removed by Granular Activated Carbon Filters	
			GAC†	Exhausted GAC‡
1	109	0.038	22	54
2	104	0.027	16	48
3	104	0.032	19	43
4	61	0.031	8	26
5	101	0.027	30	40
6	102	0.029	29	34
7	102	0.029	10	34
8	101	0.029	7	16

*Spiked Cincinnati tap water
†Filtrasorb 100, Calgon Corp., Pittsburgh, Pa.
‡Filtrasorb 200, Calgon Corp., Pittsburgh, Pa.

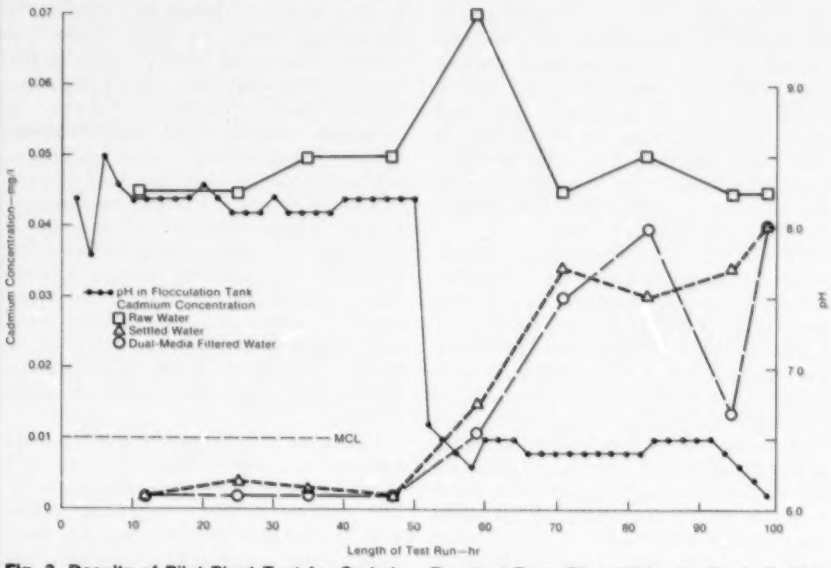

Fig. 3. Results of Pilot-Plant Test for Cadmium Removal From River Water by Ferric Sulfate Coagulation
Test No. 15; Ferric Sulfate Dose—31 mg/l

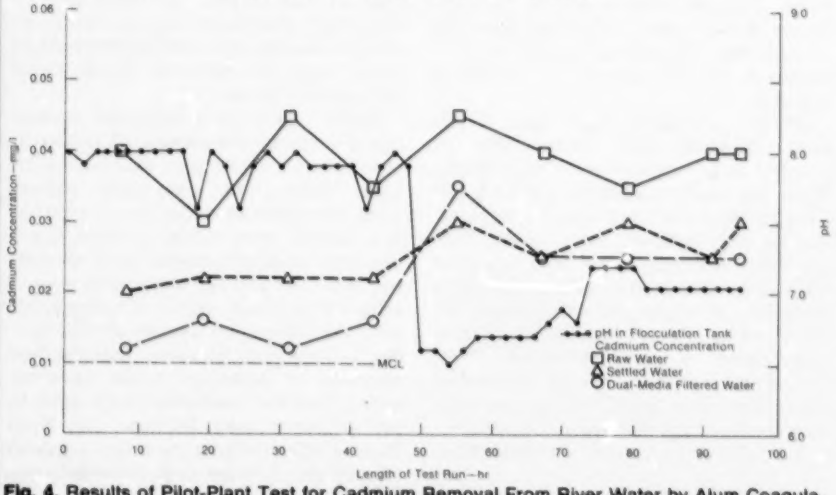

Fig. 4. Results of Pilot-Plant Test for Cadmium Removal From River Water by Alum Coagulation
Test No. 17

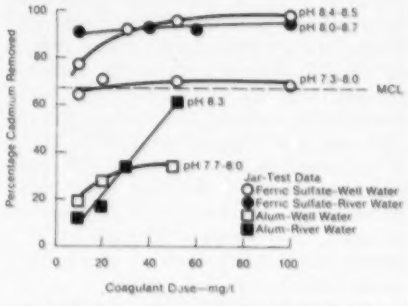

Fig. 5. Effect of Coagulant Dose on Cadmium Removal by Coagulation Treatment
Cadmium Concentration—0.03 mg/l

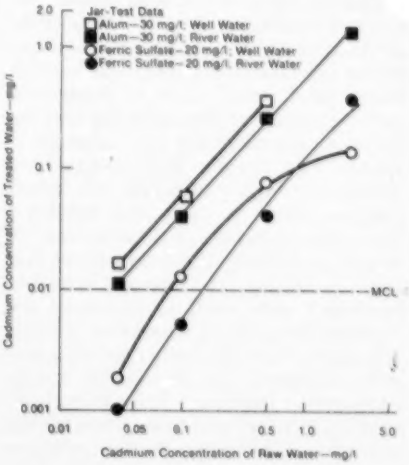

Fig. 6. Effect of Initial Concentration on Cadmium Removal by Coagulation Treatment

sis may not be as effective for cadmium removal as it is for most ions.

Little information was available on the use of electrodialysis for cadmium removal. Bovet[26] claimed this technique was successful and economical for removing cadmium from wastewater in the plating industry but listed no data.

Cadmium treatment summary. Cadmium removal by conventional coagulation treatment is pH dependent: removals increase with increasing pH. Iron coagulation is slightly more effective than alum, with greater than 90 per cent removal of environmental cadmium levels achieved at about pH 8 and above. If the water is low in alkalinity, alum removal is also dependent on turbidity: the higher the turbidity, the greater the percentage of cadmium removal. Removals can be increased by increasing coagulant dose.

Lime and excess lime softening are very effective for cadmium removal, achieving nearly 100 per cent reduction throughout the pH range from 8.7 to 11.3. Excellent removal of about 100 per cent can also be achieved with cadmium concentrations as high as 10 mg/l at pH 11.3.

Ion exchange treatment using cation exchange resins has been used in the plating industry and therefore should be effective for removing cadmium from drinking water. Standard cation resins have good selectivity for cadmium with only calcium, lead, and barium being more preferred. Cadmium removal by ion exchange may, however, be pH dependent.

Powdered activated carbon is not an efficient method for cadmium reduction because very large PAC doses (100 to 200 mg/l) will remove only small amounts of cadmium in addition to that removed by alum. Another shortcoming of PAC is the high pH (8.9) required for removal. GAC will remove moderate amounts of cadmium (30–50 per cent) and therefore may be useful for surface water treatment.

Because removal data suggest only 70 per cent reduction for low and high cadmium concentrations, reverse osmosis may not be practical for cadmium removal. Additional work is needed to clarify rejection efficiency for reverse osmosis and electrodialysis.

Because cadmium has not been reported as a major drinking water problem, very little research on its removal is planned by the DWRD. The Charlotte Harbor, Fla., reverse osmosis project described in Part 1 (JOURNAL AWWA, 70:2:105) will provide data to help clarify the question of rejection.

Lead Removal From Water

Health effects. Lead has been in the USPHS drinking water standards since 1925,[27] when the limit was first set at 0.1 mg/l. When the USPHS revised its standards in 1962,[1] the lead limit was lowered to 0.05 mg/l, mainly because the number of sources and the extent of lead exposure had steadily increased over the years. The limit was maintained by EPA in establishing the 1976 NIPDWR.[2]

Lead is well known for its toxicity, and no beneficial effects have been found on human or animal development. Although acute lead poisoning is somewhat rare, chronic lead toxicity is common because lead accumulates in bone and tissue and people are exposed to lead in food, air, and water, including that used in cooking and beverages. Another source is inhaled tobacco smoke.

The general symptoms of lead poisoning are gastrointestinal disturbances, loss of appetite, fatigue, anemia, motor nerve paralysis, and encephalopathy.[28] Because these symptoms are not unique to lead poisoning, it is often misdiagnosed. The major chronic effects are produced in the hematopoietic system, central and peripheral nervous systems, and kidneys.

A special risk group for lead toxicity is small children in the two- to three-year age group, because lead absorption from food and water at that age is 40–50 per cent as compared to 5–10 per cent for adults.[29] Furthermore, young children experience a greater risk of ingesting lead from other sources, such as lead-containing paints and dusts; lead concentration of dust in urban areas has been found to vary inversely with distance from the ground.[29]

The WHO recommends 5 μg of lead per kg per day per person as a safe total daily intake. Considering the average amount of lead intake from food and air, the NAS[29] states the interim MCL for lead in drinking water provides a very small margin of safety for certain high-risk population groups in urban areas, which are exposed to above-average lead levels in the air. Based upon the WHO recommendation, the NAS also concluded that the no-observed-adverse-health-effect level cannot be set with assurance at any value greater than 0.025 mg/l. This opinion suggests that EPA should consider lowering the MCL in the revised regulations to be promulgated in the future.

The principal problem with lead in drinking water does not result from lead in natural groundwaters or polluted surface waters, but from water distribution systems. Kopp and Kroner[11] reported 305 occurrences of lead (19.3 per cent) in 1577 samples from lakes and rivers of the US, the minimum, maximum, and mean values being 0.001 mg/l, 0.14 mg/l, and 0.023 mg/l, respectively. Durum et al[12] found that 63 per cent of 730 surface water samples had lead concentrations ranging from 0.001 to 0.05 mg/l. Very few samples had lead values greater than the 0.05-mg/l MCL. Occasionally, lead may be found in groundwaters at levels as high as 0.4–0.8 mg/l. Dutt and McCreary[31] reported that 6.5 per cent of 677 water samples collected from Arizona groundwaters had lead concentrations exceeding the MCL, with the highest recorded level being 0.518 mg/l.

The 1969 Community Water Supply study[13] showed that 37 of 2595 water distribution line samples of 969 public water supply systems contained lead concentrations exceeding the 0.05-mg/l limit. Although this survey did not indicate that lead was a serious problem in finished waters, a more recent survey[32] in the Boston, Mass., area indicated that old distribution lines containing lead-lined pipe and lead fittings can contribute significant amounts of lead in corrosive waters. Also, zinc-galvanized iron pipe, in which lead and cadmium are contaminants, and other alloy materials (such as solder, brass, and bronze) are potential sources of lead. Water samples collected from 383 households in Boston, Cambridge, and Somerville, Mass., had lead concentrations ranging from less than 0.103 mg/l to 1.51 mg/l, with the mean of all samples at 0.030 mg/l.[32] Although the MCL of 0.05 mg/l was exceeded by only 15.4 per cent of the samples, detectable levels of lead were found in 62.7 per cent of all households in the study. As expected, the highest concentrations were detected in samples collected in the early morning after water had stood overnight. The mean of all early-morning samples having detectable amounts of lead was 0.104 mg/l, which is twice the MCL. Other relationships shown in the three-community survey were higher incidences of lead detection and concentrations with the greater usage of lead pipe and with water of lower pH, hardness, and alkalinity.

Lead chemistry overview. The most significant lead complexes in water containing carbonate are carbonate ($PbCO_3$), hydroxide [$Pb(OH)_2$], and hydroxycarbonate [$Pb_3(OH)_2(CO_3)_2$]. In an Eh–pH diagram constructed by Hem and Durum,[33] the carbonate form occurs in the 5–8 pH range, the hydroxycarbonate form in the 7.5–8.5 pH range, and the hydroxide above pH 8.5. The hydroxycarbonate form occurs over so short a pH range that its significance in water treatment is minimal.

Several investigations[15,23,34] reported the solubility of lead carbonate and lead hydroxide, the least soluble common forms of lead in aqueous solutions. Although the literature indicates some conflicting values of optimum pH for the solubilities of the two forms, there is agreement that the solubility of lead is greatly affected by pH and the carbonate ion concentration of the water.

The calculated solubility graphs of Hem and Durum[33] show the solubility of lead decreasing with increasing pH to about pH 10. Above pH 8.0, the solubility

TABLE 4

Results of Conventional Coagulation Pilot-Plant Tests for Lead Removal

Test No.	Date Started	Length of Test hr	Test Water*	Coagulant Type	Coagulant Dose mg/l	pH of Treated Water	Average Raw Water Concentration mg/l	Percentage Lead Removed: Settled Water	Filtered Water: Dual-Media Filter	Granular Activated Carbon Filters: Virgin GAC†	Exhausted GAC†	Virgin GAC‡
1	12/6/76	102	Ohio River	alum	30	8.0	0.15	82	> 97	> 97	> 97	–
2	12/13/76	100	Ohio River	alum	30	6.9	0.11	86	> 96	> 95	> 95	–
3	1/17/77	92	Ohio River	ferric sulfate	30	8.0	0.20	85	96	98	98	–
4	1/24/77	72	Ohio River	ferric sulfate	24	7.0	0.20	74	98	98	98	–
5	4/4/77	102	Ohio River	alum	30	6.8	0.18	93	> 98	–	> 98	> 98
6	6/20/77	100	Ohio River	alum	30	8.2	0.18	32	90	–	97	97
7	6/27/77	50	Ohio River	alum	28	7.9	0.20	76	95	–	> 97	> 97
	continuous	45				6.9	0.18	74	90	–	> 97	> 97

*Water spiked with $PbNO_3$.
†Filtrasorb 200, Calgon Corp., Pittsburgh, Pa.
‡Hydrodarco 1030, ICI United States, Inc., Wilmington, Del.

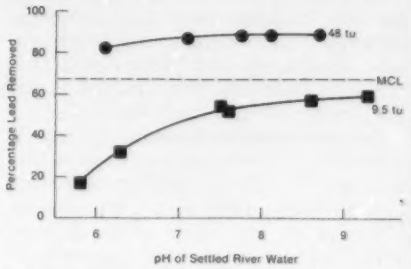

Fig. 9. Effect of Turbidity and pH on Lead Removal by Settling of River Water

Lead Concentration—0.15 mg/l

TABLE 5

Results of Conventional Coagulation Pilot-Plant Tests for Silver Removal

Test No.	Date Started	Length of Test hr	Test Water*	Coagulant Type	Coagulant Dose mg/l	pH of Treated Water	Average Raw Water Concentration mg/l	Percentage Lead Removed†: Settled Water	Filtered Water: Dual-Media Filter	Granular Activated Carbon Filter: Virgin GAC‡	Exhausted GAC‡	Virgin GAC§
1	1/31/77	94	Ohio River	ferric sulfate	29	7.8	0.16	69	> 81	> 81	> 81	–
2	3/7/77	99	Ohio River	ferric sulfate	32	6.5	0.16	81	> 81	> 81	> 81	–
3	4/4/77	102	Ohio River	alum	30	6.8	0.08	> 63	> 63	–	> 63	> 63
4	4/18/77	100	Ohio River	alum	32	6.7	0.08	27	61	–	> 63	> 63
5	4/25/77	100	Ohio River	alum	30	8.1	0.10	46	> 70	–	> 70	> 70
6	5/23/77	93	Ohio River	alum	29	7.0	0.16	59	76	–	> 81	> 81
7	6/6/77	100	Ohio River	alum	27	8.3	0.12	33	> 75	–	> 75	> 75

*Water spiked with $AgNO_3$.
†Detectable limit of 0.03 mg/l was used to compute percentage where effluent was at or below detectable limit; value reported with > symbol.
‡Filtrasorb 200, Calgon Corp., Pittsburgh, Pa.
§Hydrodarco 1030, ICI United States, Inc., Wilmington, Del.

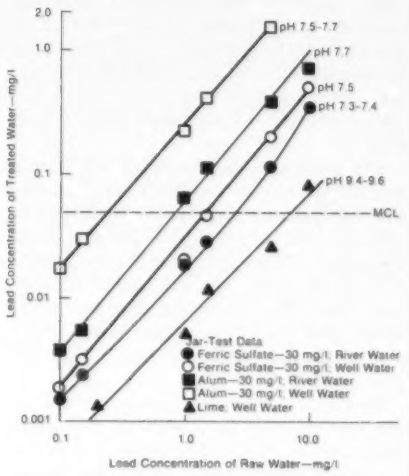

Fig. 10. Effect of Initial Concentration on Lead Removal by Conventional Coagulation and Lime Softening Treatment

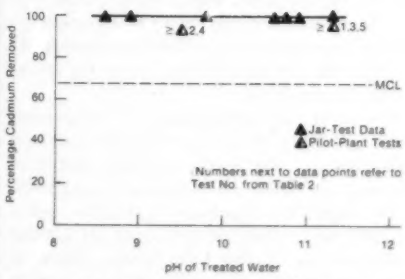
Percentage Cadmium Removed
pH of Treated Water
MCL
Jar-Test Data
Pilot-Plant Tests
Numbers next to data points refer to Test No. from Table 2

Fig. 7. Effect of pH on Cadmium Removal by Lime Softening

Cadmium Concentration—0.03 mg/l

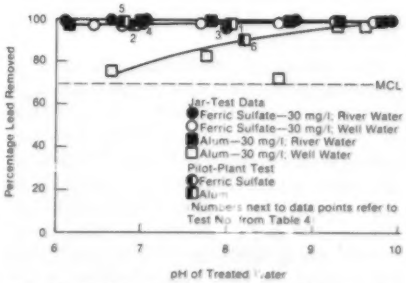

Fig. 8. Effect of pH on Lead Removal by Coagulation Treatment

Lead Concentration—0.15 mg/l

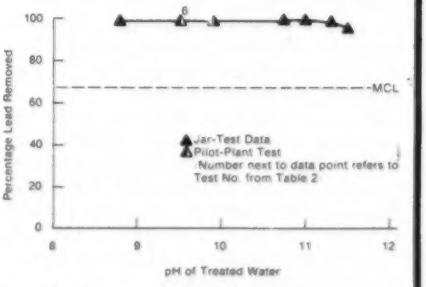
Percentage Lead Removed
pH of Treated Water
MCL
Jar-Test Data
Pilot-Plant Test
Number next to data point refers to Test No. from Table 2

Fig. 11. Effect of pH on Lead Removal by Lime Softening

Lead Concentration—0.15 mg/l

of lead is below 0.01 mg/l regardless of the alkalinity. Near pH 6.5, however, the solubility of lead could approach or exceed 0.1 mg/l. The authors suggested that water treatment processes incorporating raising the pH above 8.0 prior to filtration would decrease lead concentrations to very low levels.

Naylor and Dague[34] conducted laboratory tests to determine the effects of various parameters such as pH, hardness, and alkalinity on the solubility of lead. The soluble lead concentration could be reduced to approximately 0.1 mg/l at a pH as low as 7.6 with the alkalinity at 100 mg/l (as $CaCO_3$). With 200 mg/l of carbonate alkalinity (as $CaCO_3$), lead solubility was less than 0.01 mg/l to pH 8.6, at which point the solubility increased abruptly to 0.9–1.1 mg/l. The authors indicated that this was unexpected and concluded that physical rather than chemical parameters were the cause of the high lead levels. The explanation offered was that the colloidal particles of the insoluble lead complex, basic lead carbonate, had passed through the membrane filter. The authors also concluded that in the pH range of 5–8.5 lead precipitates predominantly as the carbonate, and between pH 8.5 and 12.5 as either lead oxide or the basic lead carbonate. Beyond pH 12.5 the more soluble lead hydroxide complex begins to form.

Patterson et al[15] determined both experimentally and theoretically the solubility of lead hydroxide and lead carbonate over the pH range 6–13 and compared the two systems. The experimental and theoretical data for lead hydroxide solubility were in agreement above pH 11, but below this point the experimental values were significantly lower than the predicted values. The difference was explained by a low carbonate concentration present in the hydroxide system. The minimum lead hydroxide solubility measured was 0.6 mg/l at pH 10.5 (total carbonate concentration of 40 mg/l). From pH 6.0 to 10.5, lead solubility was 1700 mg/l to 0.6 mg/l. Two carbonate systems were tested with high carbonate concentrations (5500 mg/l) and low carbonate concentrations (130 mg/l). The results of both tests were similar, except that better conformance of experimental to theoretical results was achieved with the low carbonate water throughout the pH range.

The optimum pHs for the three systems tested were 10.5 for the hydroxide system (0.60 mg/l of soluble lead); 10.1 for the high carbonate system (1.0 mg/l of soluble lead); and 7.5 for the low carbonate system (0.60 mg/l of soluble lead). Patterson et al[15] also observed that the carbonate precipitate had better filterability characteristics and formed a denser sludge. The potential shortcoming of lead carbonate precipitation is that lead equilibrium with the normal carbonate ion is slow.

From a water treatment viewpoint, the three studies indicate that conventional coagulation should be most effective for lead removal in the 7–8 pH range with water containing carbonate. Lime softening should also be capable of achieving high lead removal by precipitation of lead hydroxide or lead oxide.

Treatment methods. Because lead is not a widespread problem in drinking water, little research has been done on its removal. Several investigations have studied lead removal by conventional coagulation and lime softening, but only limited data exist on its removal by ion exchange, powdered and granular activated carbon, reverse osmosis, and electrodialysis.

Conventional coagulation. Alum and iron coagulation are very effective for lead removal from drinking water because lead is easily adsorbed by turbidity and forms insoluble complexes in the normal pH range for coagulation treatment. Jar-test studies by the DWRD showed that iron coagulation of river and well water and alum coagulation of river water could achieve almost 100 per cent removal of lead throughout the pH range 6–8 (Fig. 8). Alum coagulation of low-turbidity well water was slightly less effective, and lead reduction was pH dependent (Fig. 8). Lead removal increased with increasing pH, from 78 per cent at pH 6.6 to 96 per cent at pH 9.6. This same pH trend was observed by Naylor and Dague[34] in laboratory tests on alum coagulation. The absence of a pH trend with the other three test conditions was probably the result of the high turbidity of the river water and the greater effectiveness of iron floc for metal removal.

To evaluate the significance of turbidity on lead removal, two jar-test experiments were run without added coagulant. The test waters were spiked with lead, the pH of each jar adjusted with soda ash, and the water mixed for 10 min and then settled for 1 hr. Settled water samples were centrifuged to remove any remaining suspended material and the supernatant analyzed for lead. The results of the two tests on waters having turbidities of 42 and 9.5 tu are plotted in Fig. 9. Significant amounts of lead can be removed by mixing and settling, indicating that lead is easily adsorbed onto the turbidity. Furthermore, the lead reduction is dependent on the level of turbidity and pH of the water.

DWRD conducted pilot-plant tests with Ohio River water to confirm the jar-test results (Table 3). The dual-media filter results plotted on Fig. 8 show pilot-plant removal to be identical to jar-test results. Lead concentrations of the dual-media effluent water were at or below the detectable limit of 0.005 mg/l, indicating removals of nearly 100 per cent. The pilot-plant data did not exhibit a pH effect; high removals were achieved at pH 6.8 and 8.0. No test runs were conducted with well water.

In several jar-test experiments to determine the coagulant dose effect, increasing coagulant dose improved lead removal. For example, alum doses of 10, 20, 30, 50, and 100 mg/l with well water achieved 52, 72, 79, 86, and 92 per cent removals, respectively, of 0.15 mg/l of lead. Better removal results were also obtained by increasing doses of alum and iron in river water.

To evaluate the effect of the initial lead concentration on the percentage of removal, jar tests were carried out with lead concentrations of 0.15 to 10 mg/l. As expected, percentage removals decreased slightly with increasing lead concentration when all other parameters were constant. The test results (Fig. 10) show the amount of lead remaining in the treated water, demonstrating that the least effective method is alum coagulation with low-turbidity well water. With 30 mg/l of alum, the lead MCL can be achieved when the initial concentration is 0.2 mg/l or less in well water. If the drinking water source is turbid river water, the same alum dose is equally effective when the initial concentration is almost four times higher at 0.8 mg/l. Fig. 10 also shows that ferric sulfate is more effective than alum, with the MCL attainable when the initial concentration is as high as 1.5–2.5 mg/l.

Lime softening. DWRD jar-test studies showed lime and excess lime softening to be more effective than iron and alum coagulation for lead removal. Greater than 99 per cent removals of 0.15 mg/l of lead were achieved throughout the pH range 8.8 to 11.0 (Fig. 11). Although Naylor and Dague[34] indicated that lead removals may be impaired above pH 10.4, these jar-test results did not demonstrate such a problem. A possible explanation for the high removals above pH 10.4 is the large amount of calcium carbonate on magnesium hydroxide floc developed with Glendale, Ohio, well water at high pH. Greater than 99 per cent reduction was also obtained at pH 9.4–9.6 with initial lead concentrations of 10 mg/l. When these data are plotted to indicate the amount of lead remaining in the treated water, the results show that the MCL can be achieved with lead concentrations to about 7 mg/l (Fig. 10). One pilot-plant test run was completed at pH 9.5 with the results given in Table 2. The dual-media filter removal was 99 per cent, in good agreement with the jar-test data (Fig. 11).

Ion exchange. Because lead is not commonly found in groundwaters, ion exchange normally would not be considered as a treatment alternative for lead removal. However, ion exchange could

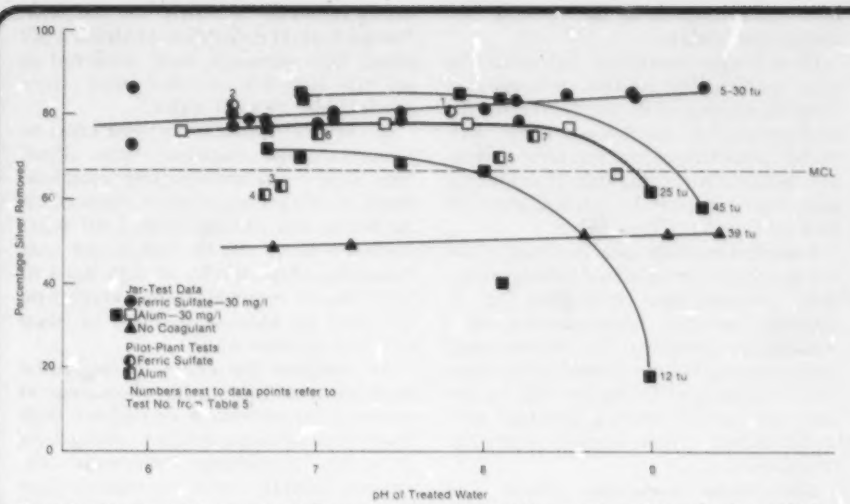

Fig. 12. Effect of pH and Turbidity on Silver Removal From River Water by Coagulation Treatment

Silver Concentration—0.15 mg/l

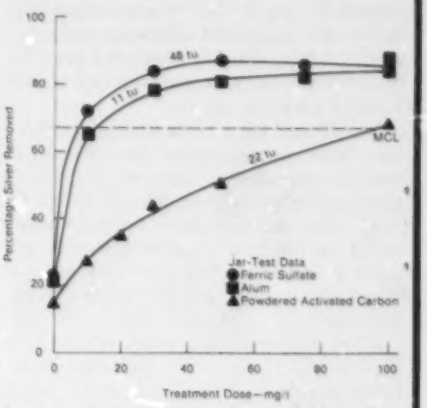

Fig. 13. Effect of Dose on Silver Removal From River Water With Ferric Sulfate, Alum, and Powdered Activated Carbon

Silver Concentration—0.15 mg/l

be important as a household method for removing lead in tap water in communities that have lead distribution line problems that cannot be solved by correcting the corrosive nature of the water. The literature indicates that lead is a highly preferred cation by strong-acid cation ion exchange resin.[17-19] Thus, ion exchange should be an effective method for lead removal. The technique is reported as a successful industrial waste treatment method, but a study by Kozak et al[35] indicates it may not be a practical method for water treatment, particularly in the home. This investigation on the removal of lead from an ammunition plant waste stream (6.5 mg/l) indicated that pH was critical. Above pH 5.2, a portion of the lead slipped though the resin as a colloid; below pH 5, the exchange capacity was reduced. If the pH of the water is significant for achieving the MCL, the method would not be practicable for drinking water treatment. Additional research is needed to determine whether lead removal by ion exchange is pH dependent.

Activated carbon. Sigworth and Smith[36] reported laboratory studies on solutions of lead nitrate and lead acetate showing little adsorption at pH 2.0 but fairly good removal at pH 5.0 with activated carbon. No specific removal data were given nor was the type of activated carbon identified. Netzer and Norman[37] studied the removal of several trace metals, including lead, at varying pH with large doses (10 000 mg/l) of PAC. In the pH range 3-5, where pH has no effect on lead solubility, lead reductions from 100 and 10 mg/l to less than 0.1 mg/l were achieved with PAC alone. At pH 5-10, the combination of pH adjustment and PAC continued to produce very high removals (greater than 99 per cent), but in this range pH adjustment was responsible for 8-84 per cent of the reduction, with removal percentage increasing with increasing pH.

In a DWRD-conducted jar test to evaluate the removal of 0.15 mg/l of le[illegible] from river water (45 tu) at pH 7.5 with PAC, varying doses of 10 [illegible] mg/l of PAC were introduced in[illegible] jars and the water stirred rapidly [illegible]. Lead measurement on centrifu[illegible] samples showed removals increasing from 89 per cent with 10 mg/l of PAC to 98 per cent with 200 mg/l of PAC. A comparison of these results to the turbidity removal results (Fig. 9) shows that PAC increases lead removals only slightly above those achieved by turbidity removal alone.

Although GAC may be effective for lead removal, the DWRD pilot-plant studies showed such high removals by conventional coagulation treatment that no advantages are seen for lead removal by substituting GAC for dual-media filtration for surface water treatment. No other information was found on the removal of lead from water by GAC.

Reverse osmosis and electrodialysis. When Mixon[23] studied the removal of lead from tap water by reverse osmosis (RO), greater than 99.5 per cent removal of 0.95 mg/l was achieved by three types of cellulose acetate membranes. When the lead concentration was increased to 9.3 mg/l, lead rejections were 94.6 to 97.8 per cent. High lead removals (above 99 per cent) were also achieved with tap water containing a mixture of lead (4.75 mg/l) and five other metals. Mixon reported that RO testing of lead in secondary clarifier effluent and in sludge plant clarifier effluent was not feasible because the lead formed an insoluble precipitate. Although no specific rejection information was found in the literature on lead removal from drinking water by electrodialysis, this technique should be as effective as RO.

Lead treatment summary. Because lead forms insoluble hydroxide and carbonate complexes, coagulation and lime softening treatment are both effective methods of removing lead from water. Except for alum coagulation of well water, laboratory studies and pilot-plant tests showed that lead removal by these treatment techniques is not pH dependent; 99 per cent removal can be achieved from pH 6.5 to 8.5 for coagulation treatment and from pH 9.5 to 11.3 for lime softening on environment levels of lead. Although alum is as effective as iron coagulants in river water, it was slightly less effective than ferric sulfate with well water. Moreover, a slight pH removal trend exists with alum coagulation of well water. Increasing coagulant dosage improves lead removal.

The percentage of lead removal is dependent on the initial concentration for conventional coagulation and lime softening treatment. When high lead concentrations occur, lime softening is more effective than coagulation treatment, with 99 per cent removal capability for 10 mg/l of lead.

Test data indicate that lead is readily adsorbed onto suspended material and therefore is more easily removed from surface water than from groundwaters. PAC can achieve some lead removal, but data are lacking on the removability of lead by GAC. Limited data indicate that reverse osmosis and electrodialysis should be effective methods for lead reduction. Although ion exchange selec-

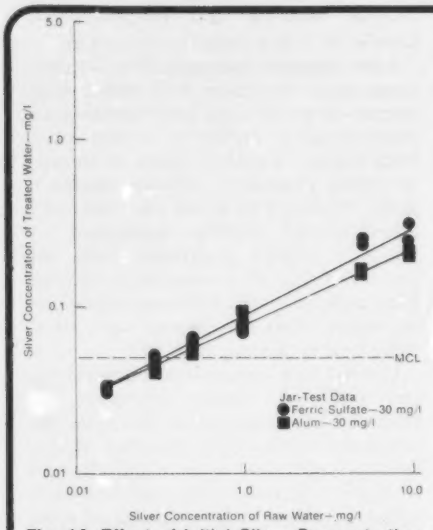

Fig. 14. Effect of Initial Silver Concentration on Silver Removal From River Water by Coagulation Treatment

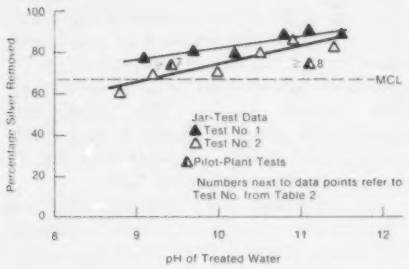

Fig. 15. Effect of pH on Silver Removal by Lime Softening

Silver Concentration—0.15 mg/l

tivity information shows lead to be a highly preferred cation, removal may be pH dependent with best removals achieved near pH 5. At higher pH, lead penetrates through the resin bed in a colloidal form.

Because the major potential problem of lead in drinking water is leaching from service lines and plumbing, future DWRD research will study the relationship of corrosive water to lead leaching and methods to eliminate the problem.

Silver Removal From Water

Health effects. Silver was introduced into the USPHS Drinking Water Standards[1] in 1962, with a limit of 0.05 mg/l established as grounds for rejecting a water supply. The reason for introducing silver into standards was to prevent the addition of excessive amounts of silver to water for disinfection purposes. For the same reason, EPA retained silver in the NIPDWR[2] at the same level.

The principal effect of silver on the body is cosmetic. Silver causes an unsightly permanent blue-grey color of the skin, eyes, and mucous membranes. The amount of silver required to produce this condition (argyria) is unknown, but the amount of silver from injected Ag-arsphenamine, a substance which produces argyria, is precisely known to be any amount greater than 1 g of silver, 8 g Ag-arsphenamine, in an adult.[38,39]

A study of the toxicological effects of silver on rats, in which silver was added to drinking water at concentrations to 1 mg/l, showed pathological changes in kidneys, liver, and spleen at 0.4, 0.7, and 1 mg/l, respectively.[40] The major evidence for concern about silver is that once it is absorbed, it is held indefinitely in tissues, particularly the skin. In addition to the silver ingested from drinking water, it is assumed that silver can also be ingested from certain vegetables, such as cabbage, turnips, cauliflower, and onions, that would combine with residual silver in the cooking water. In 1940 a study[41] indicated that 0.06–0.08 mg per day was absorbed from water cooked in silver-containing waters, indicating high absorbability of silver bound to sulfur components in food.

When the NAS[29] reviewed the silver health effects information for EPA, their report did not recommend any change in the silver limit for drinking water.

Silver should not be a problem in either natural groundwaters or surface water except in a few isolated cases. Kopp and Kroner[11] reported less than 7 per cent of 1577 samples from their rivers and lakes survey had detectable amounts of silver, with a maximum value of 0.038 mg/l and a mean of 0.0026 mg/l. The 1969 Community Water Supply Survey[13] showed that none of the finished waters sampled exceeded the 0.05-mg/l limit; the maximum concentration was 0.03 mg/l.

Silver chemistry overview. In natural waters silver occurs as the free ion, Ag^+ and possibly as soluble AgSH, $Ag(SH)_2^-$, and $Ag_2S_3H_2^{-2}$.[42] Silver is also associated with suspended material in water.

The literature[43] indicates that the formation of silver hydroxide is doubtful, as contrasted to evidence for many other metals. In alkaline solutions, if silver hydroxide does precipitate, the complex is unstable and decomposes to the slightly soluble oxide species, AgO. In contrast to most metal chlorides, which are relatively soluble, silver chloride is extremely insoluble, and the precipitation of this complex is used in the wastewater field to remove silver. Silver sulfide is another very insoluble compound; although the use of sulfide to precipitate silver from solution has been successfully utilized by the photographic industry, the mechanism is not practical for water treatment.

Krauskopf[44] studied the factors controlling the concentration of silver and twelve other metals in sea water: (1) precipitation of sulfide complexes; (2) precipitation of insoluble compounds with ions normally present in aerated sea water; (3) adsorption by ferrous sulfide, hydrated ferric oxide, hydrated manganese dioxide, apatite, clay, plankton, and peat moss. Surprisingly, only the organic materials—plankton and peat moss—adsorbed significant amounts of silver. For example, with sea water containing about 0.5 mg/l of silver, plankton achieved 96 per cent adsorption as compared to 15 per cent for hydrated ferric oxide and 8 per cent for hydrated manganese dioxide. Although Krauskopf indicated several shortcomings in the experimental procedures, the data definitely revealed a significant difference between the adsorption of silver by organic and nonorganic materials. The data suggest that silver should be readily adsorbed onto organic material in surface waters and either settle out with the bottom sludges or be removed by conventional treatment processes.

Treatment methods. Because silver is not a serious problem in drinking water, very little study has been devoted to its removal. Conventional coagulation and lime softening treatment have been investigated by the DWRD, and very limited data also exist on the use of the same methods in the wastewater field. A general literature review found no specific studies on silver removal by reverse osmosis, electrodialysis, ion exchange, or activated carbon.

Coagulation treatment. The DWRD ran laboratory jar-test and pilot-plant studies for silver removal from Ohio river water by conventional coagulation treatment. The results of jar-test experiments to evaluate the effect of pH are shown in Fig. 12. In the 6 to 8 pH range neither alum nor iron coagulation exhibited any significant pH effect on silver removal. Above pH 8, however, alum coagulation removal results decreased sharply; one test showed silver removal of about 20 per cent at pH 9. Poor floc formation is suggested as the major reason for the decrease. Subsequent jar tests also showed that alum removals through the pH range 6 to 9 were slightly dependent on the turbidity of the river water. The higher the turbidity of the raw river water, the greater the reduction of silver (Fig. 12). Repetitive iron coagulation tests did not show the turbidity effect; silver removals were 55–65 per cent with river water having a turbidity of 5–30 tu.

Because of the observed turbidity

effect on silver reduction with alum coagulation, a jar test was performed with no coagulant. River water was spiked with 0.15 mg/l of silver, the pH was adjusted with soda ash from pH 6.8 to 9.4, and the water was mixed for 1 hr. Collected water samples were centrifuged and the silver concentration of the supernatant liquor measured. The results, which are plotted in Fig. 12 for comparison to the coagulation treatment removals, showed a silver reduction range from 49 to 56 per cent and no pH effect. The data indicate that silver readily adsorbs onto suspended material and that settling alone could remove a significant amount of silver.

Pilot-plant tests run with the same river water to verify the jar-test data are summarized in Table 5. Alum coagulation tests were repeated several times because of problems in obtaining the desired silver level in the raw water. Although the silver contaminant feed was set for 0.15–0.18 mg/l in the raw water, the measured amount was often recorded at about one half the theoretical concentration. One possible explanation lies with the analytical method's (atomic adsorption) not measuring the total silver amount because of the high turbidity in the raw water (60–150 tu). Based upon measured silver concentrations, silver removals were generally above 70 per cent for all test conditions. Because the minimum detectable limit of silver was 0.03 mg/l, more precise removal calculations could not be made. Higher resolution was attainable in the jar-test studies because radioisotope tracer methods were employed to determine silver removal.

Little improvement in silver removal can be achieved by increasing the coagulant dose of ferric sulfate or alum above 30 mg/l (Fig. 13). Jar-test results showed only a 5–10 per cent increase with coagulant doses of 100 mg/l and very little difference in removals between the two coagulants. Silver removal results of the two coagulants were also similar in jar tests evaluating the effect of initial silver concentration. Although total percentage removals increased as raw water silver concentration increased, the concentration in the treated water also continued to rise (Fig. 14). These data indicate that the silver MCL of 0.05 mg/l can be achieved with 30 mg/l of coagulant when the initial concentration is about 0.35 mg/l or less. If the raw water concentration is above this, other measures must be used to obtain higher removals.

Lime softening. Jar-test and pilot-plant studies on silver removed by lime softening show this treatment method to be moderately effective and comparable to coagulation treatment. Two jar-test experiments were run; removals in each test were slightly different but a similar removal trend showing increase with pH was achieved (Fig. 15). Because of the 0.03-mg/l minimum detectable limit of silver, pilot-plant data could not be precisely calculated. The silver concentrations of the effluent water of the dual-media filter were below 0.03 mg/l, and thus the calculated removal values (> 74 per cent) were equal to or greater than the jar-test results. The pilot-plant results are given in Table 2, and dual-media filter results are plotted in Fig. 15 for comparison to jar-test data.

Ion exchange. The literature has no specific data on ion exchange treatment for silver removal from drinking water, but Linstedt et al[21] reported silver (0.055 mg/l) reductions from secondary wastewater of 85.8 per cent by cation exchange and 91.7 per cent by cation and anion exchange in series. Silver has also been removed from industrial waste solutions by ion exchange treatment. Silver is highly preferred by strong-acid cation exchange resins. Calmon[18] stated that silver in a noncomplexed form can be removed easily by a cation exchanger.

Activated carbon. A DWRD jar test on Ohio river water spiked with 0.15 mg/l of silver showed low removals by PAC (Fig. 13). Removal increased with increasing doses of PAC, but the best results were only 66 per cent with 100 mg/l PAC. Sigworth and Smith,[36] however, report laboratory studies on silver nitrate solution showing that activated carbon could adsorb 9 per cent of its own weight at pH 2.1 and 12.5 per cent at pH 5.4. No data were presented on removal at high pH, but the authors suggested good potential for removal. Very high silver removals from wastewater by PAC were also reported by Netzer and Norman.[37] Removals of more than 99.9 per cent of 100 mg/l and 10 mg/l of silver were obtained from pH 3 to 11. Very high PAC doses (10 000 mg/l) were used, thus indicating only a potential use of PAC for water supply treatment.

The detection limitation prevented an assessment of the adsorbability of GAC for silver removal from the data of Table 5. The only conclusion that can be drawn is that removals by the GAC filters were at least equivalent to those by dual-media filters. Whether higher silver removals were achieved by GAC filters is not known. Linstedt et al,[21] who studied silver removal from wastewater, reported high removal efficiency for silver by GAC. Cumulative removals of trace amounts of silver (1.66 μg/l) by sand filtration followed by GAC were 11.6 and 97.1 per cent respectively.

Reverse osmosis and electrodialysis. No data were found in the literature on silver removal from drinking water by reverse osmosis or electrodialysis. An equipment manufacturer's literature[43] on meeting the drinking water regulations by reverse osmosis lists an estimated removal range of 93–95 per cent. Both reverse osmosis and electrodialysis should be able to achieve this range.

Silver treatment summary. Conventional coagulation treatment with either alum or iron coagulants and lime softening are about equal in ability to remove silver from water. Coagulant doses of 30 mg/l of either coagulant achieve moderate silver removals of 60–80 per cent, with alum results slightly dependent on turbidity. Higher coagulant doses improve removal by a very small amount. Lime softening also achieves removal in the range of 60–85 per cent, with silver reduction increasing with pH.

Limited data suggest that ion exchange and activated carbon treatment are effective but impractical methods for removing silver from drinking water. Reverse osmosis and electrodialysis should be efficient because of their abilities to achieve high rejections of most heavy metals. Silver is not a serious problem in US drinking water; thus no research on its removal from water supplies is planned for the immediate future by the DWRD.

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The Use of Particle Counting in Developing Plant Design Criteria

Carol H. Tate and R.R. Trussell

Turbidity measurement has traditionally been a primary indicator of treatment effectiveness, but turbidity is an indirect measurement that does not always provide the complete information sought from pilot-plant investigations. The authors report on their evaluation of particle-counting techniques, which have been found to be useful in pilot-plant process evaluation and optimization.

Recent events in the water supply field have emphasized the need to provide consumers with water of low turbidity. With the passage of the Safe Drinking Water Act[1] in 1974, development of national water quality standards was mandated. Accordingly, the USEPA in 1975 published the National Interim Primary Drinking Water Regulations,[2] which took effect in June 1977. For the first time on a nationwide basis the standards for drinking water included a mandatory rather than recommended limit for turbidity.

The turbidity standard is based on the fact that turbidity can have effects on health as well as on esthetics. It has been demonstrated that turbidity can interfere with disinfection. For example, Symons and Hoff[3] have shown that turbidity can interfere with disinfection of viruses, presumably because the particulate material responsible for turbidity also has the capability of shielding these microorganisms from the disinfectant action.

Following the promulgation of a mandatory turbidity standard designed to protect public health it became necessary for many water utilities to investigate processes to produce a water of lower turbidity at reasonable cost. In many cases the selection of optimum water treatment processes has been aided by pilot-plant work. With a pilot plant it is possible to examine unit processes in detail and to optimize each process before developing design criteria for a full-scale plant.

Traditionally, one of the primary indicators of water treatment effectiveness has been turbidity. Reduction in turbidity or attainment of a given turbidity

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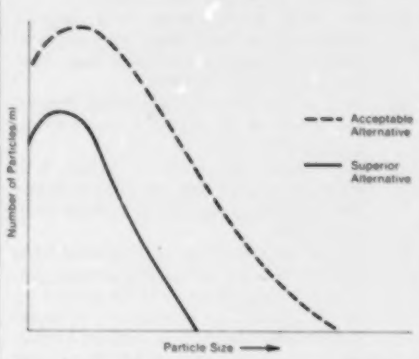

Fig. 1. Frequency Distribution of Particle Sizes: Hypothetical Demonstration of Improved Treatment

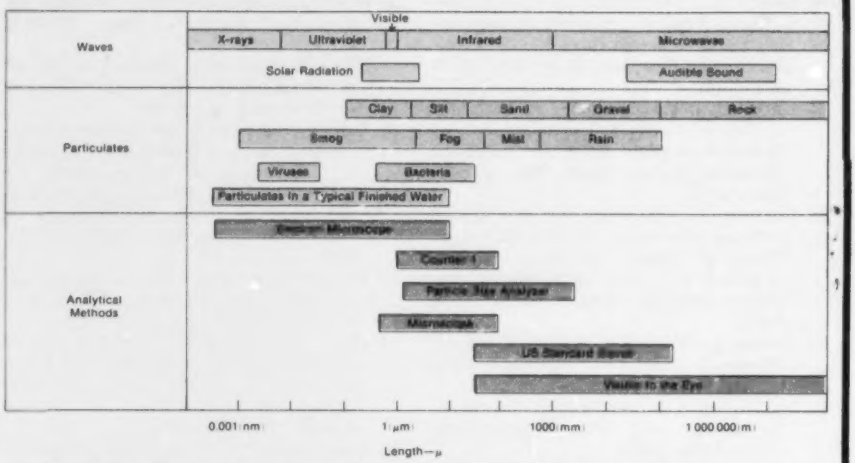

Fig. 2. Size Range and Analytical Methods for Detecting Particulate Matter in Water

objective has been practiced in pilot plants and full-scale plants. Although widely used, turbidity is an indirect measurement that does not always provide the complete information sought from pilot-plant investigations. Therefore, the authors have evaluated other direct measurements of particulate matter and have used particle-counting instrumentation in recent pilot-plant studies. In conjunction with other measurements such as turbidity, the particle-counting technique has been a useful tool in pilot-plant process evaluation and optimization.

The rationale for using particle counting and the selection of an appropriate technique are discussed in this article. Also included are results from a survey on particulate removal capabilities of existing water treatment plants and on setting a reasonable particle count objective for treated water from a pilot plant. Applications of particle counting in process studies are discussed, based on recent pilot-plant investigations with the Central Utah Water Conservancy Dist.[4] and the Los Angeles Dept. of Water and Power.[5] Most of the data presented here are taken from the latter study.

Rationale for Measuring Particle Counts

Particle counts can be a useful tool in water treatment testing because, in comparison to turbidity, they provide a direct measurement of particulate material, enhanced sensitivity, a potential for improved operational control, and a basis for assurance of disinfection.

Direct measurement. Particle counts are a direct measure of particulate material present in water. Instrumentation is available that uses light blockage, conductivity, or other techniques to analyze directly the number of particles in a given volume and to determine their size. On the other hand, turbidity is an indirect or surrogate measurement of particulate material based on the light scattered by particles. Such scattering is a function of particle size, shape, refractive index, number, and other factors.[6] A turbidity reading is related to the total light scattered by particles in the sample, but it provides no information on particle size distribution. Because of the complex nature of light scattering by particles, two water samples with equal turbidity measurements do not necessarily contain the same number of particles or the same size distribution.

Enhanced sensitivity. Comparisons of particulates in water before and after treatment processes are more meaningful when particle counts are used. For example, relatively small changes in turbidity are often accompanied by more significant changes in particle number or size distribution. This information can be used to understand more fully the mechanisms of water treatment processes.

Potential for improved operational control. Particle counts can be a sensitive parameter for process control. Such a method of quality control could be used to ensure optimal chemical dose and thus produce a chemical cost savings while achieving a given water quality objective. Similarly, more precise control could establish optimal flocculation energy input with possible savings in energy costs. The potential for using particle counts to improve operational control in pilot plants is discussed in more detail in later sections of this article. Possibilities for controlling full-scale plants have been noted by Beard and Tanaka.[7]

Assurance of disinfection. The need for a convenient measure of particulates in water has been expressed previously,[3] together with the rationale that particulates could under some circumstances protect pathogens from a disinfecting agent. With particle-counting techniques, particularly with information on size distribution, it is possible to have a greater assurance of disinfection. Figure 1 illustrates the concept using particle size distribution in water. For optimal disinfection the superior alternative is one with fewer and smaller particles.

Analytical Techniques for Particle Counting

Analytical techniques for measuring particulate material in water are related to particle size and physical-chemical characteristics. Figure 2 shows the size ranges of particulate materials and familiar wavelengths of comparable magnitude. For particulates of the size found in raw or finished water, analytical techniques include observation by light or electron microscopes and instruments based on light blockage, conductivity, or other techniques.

Microscopic techniques. Counting particles in water by a microscopic technique provides a direct measurement of particulate material within the size constraints of the microscope. A microscopic technique is the standard method for quantifying planktonic particulates.[8] Various counting cells, such as calibrated hemacytometers, are available for microscopic particle counting. A variation of microscopic particle counting involves membrane filter collection before analysis, in which case the membrane filter can serve as a permanent record of the sample. In general, microscopic techniques count plankton or other particulates per millilitre but do not produce size distribution data. Where particle